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TRUNCATED REACTION OPERATORS

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ABSTRACT   *14396*

The reaction operator formulation for the exact solution of the
Schrödinger equation is used with a truncated basis set to obtain
approximate solutions. The relationship between this truncated reaction
operator formalism and the Rayleigh-Ritz variational method is emphasized
and shown explicitly. The truncated reaction operator and its matrix
elements are discussed in general; computed and discussed for a simple
example, the helium atom, using a three membered basis set. It is
shown that the reaction operator can be replaced by a function which we
call the "effective" perturbation. This function has very fundamental
significance and may lend itself to accurate empiricism. Expressions
are given comparing the "effective" perturbation with the perturbation
and approximations to this function for the helium atom are computed.

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TRUNCATED REACTION OPERATORS

1. Introduction

Watson[1], Brueckner and Levinson[2], Löwdin[3] and others[4] have derived the reaction operator formulation for the exact solution of the Schrödinger equation. This formulation can be used with a truncated basis set to obtain approximate solutions of the Schrödinger equation. One of the purposes of our present discussion is to emphasize and show explicitly, in the simplest possible manner, the relationship between the approximate solutions obtained with a truncated reaction operator formalism and the solutions obtained by the Rayleigh-Ritz variational method. The approximate reaction operator and its matrix elements are discussed in general and in connection with a simple example, i.e. the helium atom, using a three membered basis set.

The reaction operator can be replaced by a function, V_{eff} , which we call the "effective" perturbation. It appears to us that this function has very fundamental significance. Ultimately after we have obtained a backlog of numerical and theoretical experience with the determination of the "effective" potentials for atomic and molecular problems, we may be able to accurately empiricize V_{eff} , thus obtaining good values for the energy and other physical observables of these systems.

First, consider that part of the reaction operator formulation for the exact solution of the Schrödinger equation pertinent to this paper. We fix our attention on the effect of the perturbation V on the q-th unperturbed state. The q-th state is considered to be non-degenerate and is not necessarily the ground state. The Hamiltonian for the unperturbed system is H_o and

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[1] K. M. Watson, Phys. Rev. __89__, 575 (1953).

[2] K. A. Brueckner and C. A. Levinson, Phys. Rev. __97__, 1344 (1955).

[3] P. O. Löwdin, J. Math. Phys. __3__, 969 (1962).

[4] A more complete list of references is given in K. Kumar, "Perturbation Theory and the Nuclear Many Body Problem" (North-Holland Publishing Co., Amsterdam, 1962).

$$H_o \varphi_k = E_k^{(o)} \varphi_k \qquad , \ k=1,2,\cdots \qquad , \tag{1}$$

where φ_k and $E_k^{(o)}$ are the normalized eigenfunction and eigenvalue, respectively, for the k-th unperturbed state. For the perturbed system, the Hamiltonian H , is given by

$$H = H_o + V \qquad . \tag{2}$$

The reaction or energy shift operator, t , is defined by

$$E_q = E_q^{(o)} + \left\langle \varphi_q | t | \varphi_q \right\rangle \tag{3}$$

where E_q is the exact energy for the perturbed system. Let us define two projection operators, O and P , such that

$$O \chi = \varphi_q \tag{4}$$

and

$$P = 1 - O \tag{5}$$

where χ is a trial function. Using these definitions it can be shown that the hermitian operator t , associated with V , H_o , and the state under consideration q , is given by[3]

$$t = V + VT_o t \tag{6}$$

where

$$T_o = P \left[\alpha \cdot O + P(E_q - H_o)P \right]^{-1} P \qquad . \tag{7}$$

Here α is an arbitrary number which insures the existence of the inverse operator in Eq. (7).

The exact wave function for the perturbed state, ψ_q , is given by[3]

$$\psi_q = W \varphi_q \tag{8}$$

where W is the wave operator associated with the q-th unperturbed state;

$$W = 1 + T_o t = (1/V)t \quad . \tag{9}$$

Here

$$\langle \varphi_q | \psi_q \rangle = 1 \tag{10}$$

and hence the wave function, ψ_q , has not been normalized to unity.

One may define an "effective" perturbation, $V_{eff}(q)$, which replaces the operator t in the above formulation;

$$V_{eff}(q) = (t \varphi_q)/\varphi_q \quad . \tag{11}$$

Clearly the exact energy and wave function for the perturbed system may be written as

$$E_q = \langle \varphi_q | H_o + V_{eff}(q) | \varphi_q \rangle \tag{12}$$

and

$$\psi_q = (V_{eff}(q)/V) \varphi_q \quad . \tag{13}$$

In Secs. 2 and 3 $V_{eff}(q)$ is compared with the perturbation V . In Sec. 4 approximations to $V_{eff}(q)$ for the helium atom are computed. It is our hope that the function $V_{eff}(q)$ will lend itself to empiricism.

2. Truncated Reaction Operators and the Approximate Solution of the Schrödinger Equation.

In this section we limit consideration to trial functions which may be expanded in terms of a truncated basis set, $\{\varphi_k\}$, of n eigenfunctions of an H_o . For this choice of trial function t is equivalent to a truncated reaction operator, t(n) which involves only the set $\{\varphi_k\}$. (The use of an arbitrary truncated basis set, $\{\omega_k\}$, is discussed briefly in Sec. 3; but the treatment is more

complicated.) The matrix elements of $t(n)$ are obtained by an iterative procedure, after which approximations to the energy, $E_q(n)$, and the normalized wave function, $\Psi_q(n)$, can be easily calculated. Finally an expression for the approximate "effective" perturbation, $V_{eff}(q,n)$, is obtained.

For the class of trial functions which are linear expansions in the truncated set $\{\varphi_k\}$, the operator P is equivalent to

$$P(n) = \sum_{\substack{k=1 \\ k \neq q}}^{n} |\varphi_k\rangle \langle \varphi_k| \tag{14}$$

with $O + P(n) = 1$. Using Eq. (14) we may write

$$T_o(n) = P(n)/(E_q(n) - H_o) \tag{15}$$

where the inverse operator in Eq. (15) is well defined assuming $E_q(n)$ does not equal any of the eigenvalues $E_k^{(o)}$. Using Eqs. (1), (3), (6), (14) and (15) we obtain

$$t(n) = V + V \sum_{\substack{k=1 \\ k \neq q}}^{n} \frac{|\varphi_k\rangle \langle \varphi_k| t(n)}{(E_q(n) - E_k^{(o)})} \tag{16}$$

and

$$E_q(n) = E_q^{(o)} + \langle \varphi_q| t(n) |\varphi_q\rangle \quad . \tag{17}$$

The approximate wave operator, $W(n)$, may be obtained from Eqs. (9) and (16);

$$W(n) = (1/V) t(n) \tag{18}$$

Using Eqs. (8) and (18), the normalized approximate perturbed wave function is given by

$$\Psi_q(n) = \sum_{k=1}^{n} C_{kq}(n) \varphi_k \tag{19}$$

where

$$C_{kq}(n) = Nt_{kq}(n)/(E_q(n) - E_k^{(o)}) \tag{20}$$

and

$$N = \left\{ \sum_{m=1}^{n} \left[t_{mq}(n)/(E_q(n) - E_m^{(o)}) \right]^2 \right\}^{-\frac{1}{2}} . \tag{21}$$

Thus both $E_q(n)$ and $\Psi_q(n)$ are easily obtained once the $t_{kq}(n)$ are computed.

The matrix representation of $t(n)$, using Eq. (16), is

$$t_{sq}(n) = \sum_{k=1}^{n} V_{sk} t_{kq}(n)/(E_q^{(o)} + t_{qq}(n) - E_k^{(o)}) \quad , \quad s=1,\cdots,n . \tag{22}$$

The system of equations given by Eq. (22) may be solved iteratively. A guess is made for $t_{qq}(n)$. Then the system of equations

$$t_{sq}(n) = \sum_{k=1}^{n} V_{sk} t_{kq}(n)/(E_q^{(o)} + t_{qq}(n) - E_k^{(o)}) \quad , \tag{23}$$

$$s=1,\cdots,q-1,q+1,\cdots,n \quad ,$$

is solved for the $t_{kq}(n)$'s with $k \neq q$. These $t_{kq}(n)$'s are then used in the expression

$$t_{qq}(n) = \sum_{k=1}^{n} V_{qk} t_{kq}(n)/(E_q^{(o)} + t_{qq}(n) - E_k^{(o)}) \tag{24}$$

to calculate a new value for $t_{qq}(n)$. This procedure is repeated until self consistency is obtained. From the final values for the $t_{kq}(n)$, the approximate perturbed energy and normalized wave function are given by Eqs. (17) and (19) respectively[5]. Similar iterative methods are

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[5] Solutions may also be obtained for the reaction operator matrix elements $t_{k\ell}(n)$, with $\ell \neq q$, using Eq. (16). These matrix elements, however, do not have any obvious application in the formulation for non-degenerate states. Here it should be remembered that the t-operator is defined with respect to the state under consideration, q.

available for solving the secular equation of the linear variational method, where the variational coefficients are treated in much the same way as the $t_{kq}(n)$ (see Sec. 3 and for example ref. 6).

The connection between the approximate "effective" perturbation, $V_{eff}(q,n)$, and V is obtained using Eqs. (11) and (16);

$$V_{eff}(q,n) = (t(n)\varphi_q)/\varphi_q = (V/\varphi_q)\sum_{k=1}^{n} t_{kq}\varphi_k/(E_q(n) - E_k^{(o)}) .$$

(25)

This function, $V_{eff}(q,n)$, is equivalent to the operator $t(n)$ in the computation of the energy and wave function of the perturbed system (see Sec. 1); indeed $t_{kq}(n) = (V_{eff}(q,n))_{kq}$. An approximate "effective" perturbation is computed for a specific example, the He atom, in Sec. 4. In Sec. 3 an expression for $V_{eff}(q,n)$ is obtained in terms of an arbitrary basis set $\{\omega_k\}$.

3. The Reaction Operator and the Variational Method

The reaction operator formulation is closely connected to the linear variational method for solving the Schrödinger equation. This property, is of course, implicit in the derivation of the reaction operator[3].

From Eq. (22) one obtains

$$\sum_{k=1}^{m} \left[V_{sk} - (E_q(n) - E_k^{(o)})\delta_{ks}\right] t_{kq}(n)/(E_q(n) - E_k^{(o)}) = 0 ,$$

(26)

$$s=1,2,\cdots,n .$$

The matrix element of the perturbed Hamiltonian, H_{sk}, is given by

$$H_{sk} = (H_o + V)_{sk} = E_k\delta_{ks} + V_{sk} .$$

(27)

Hence Eq. (26) becomes

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[6] P. O. Löwdin, J. Molecular Spectrosc. 10, 12 (1963).

$$\sum_{k=1}^{n} \left[H_{sk} - E_q(n) \delta_{ks}\right] t_{kq}(n)/(E_q(n) - E_k^{(o)}) = 0 \quad , \quad (28)$$

$$s=1,2,\cdots,n \; .$$

This set of equations has a non-trivial solution only if the determinantal equation

$$|D_{sk}| = 0 \quad , \quad (29)$$

where

$$D_{sk} = (H_{sk} - E_q(n) \delta_{ks})(E_q(n) - E_k^{(o)})^{-1} \quad (30)$$

is satisfied. The factor $(E_q(n) - E_k^{(o)})^{-1}$, common to each member of the k-th column, may be divided out of the determinant given by Eq. (29). Thus we obtain

$$\left[\prod_{j=1}^{n}(E_q(n) - E_j^{(o)})^{-1} \right] |H_{sk} - E_q(n) \delta_{ks}| = 0 \quad . \quad (31)$$

Since the product factor is not zero, Eq. (31) reduces to the usual secular equation[7]

$$|H_{sk} - E_q(n) \delta_{ks}| = 0 \quad . \quad (32)$$

The relationship between the linear variational coefficients, $C_{kq}(n)$, and the matrix elements of the reaction operator, $t_{kq}(n)$, is given by Eq. (20). This formula is valid only for a basis set composed of orthonormal eigenfunctions of H_o .

Arbitrary Truncated Basis Set. Consider an orthonormal truncated basis set, $\{\omega_k\}$, with the single restriction that $\omega_q = \varphi_q$. Using this basis set we may write

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[7] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids" (John Wiley and Sons, Inc., New York, 1954) p. 63.

$$t(n) = V + V \sum_{\substack{k=1 \\ k \neq q}}^{n} \frac{|\omega_k\rangle \langle \omega_k| t(n)}{(E_q(n) - H_o)} \quad . \tag{33}$$

Here, however, we may not replace H_o by $E_k^{(o)}$ as was done previously when the set $\{\varphi_k\}$ was used. On this account, there is no simple theory such as that developed in Sec. 2. On the other hand it is easy to obtain the relationship between the $C_{kq}(n)$ and the matrix elements of the reaction operator.

Let us expand the normalized wave function, $\Psi_q(n)$, in terms of the basis set $\{\omega_k\}$,

$$\Psi_q(n) = N\psi_q(n) = N \sum_{k=1}^{n} b_{kq}(n)\omega_k = \sum_{k=1}^{n} C_{kq}(n)\omega_k \tag{34}$$

where N is a normalization constant. Using Eqs. (8), (18) and (34) we obtain

$$t(n)\varphi_q = V\psi_q(n) = V \sum_{k=1}^{n} (C_{kq}(n)/N)\omega_k \quad . \tag{35}$$

Thus the general expression for the $t_{sq}(n)$ in terms of the $C_{kq}(n)$ becomes

$$t_{sq}(n) = \sum_{k=1}^{n} (C_{kq}(n)/N)V_{sk} \quad , \quad s=1,2,\cdots,n \quad . \tag{36}$$

Using Eq. (35) one may obtain an expression for $V_{eff}(q,n)$;

$$V_{eff}(q,n) = (V/\varphi_q) \sum_{k=1}^{n} (C_{kq}(n)/N)\omega_k \quad . \tag{37}$$

Equations (36) and (37) contain Eqs. (22) and (25) as special cases.

4. An Example, the Helium Atom[8]; Discussion.

We now consider a simple example to illustrate some of the ideas

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[8] A more detailed version of this work is available in the technical report, WIS-TCI-10, Theoretical Chemistry Institute, University of Wisconsin, 25 February 1963.

developed in the preceding part of this paper. The truncated reaction operator matrix elements are obtained for the $(1s)^2, (1s)(2s), (2s)^2$ ^{1}S states of helium. Simple basis sets are used, which consist of one or more configurational interaction wave functions, constructed from products of uniformly scaled hydrogen 1s and 2s orbitals. The approximate "effective" perturbation, $V_{eff}(q,n)$, is computed for specific examples. Finally, the results obtained for helium and the more general results of the previous parts of this paper are discussed.

The two electron problem is very advantageous for this investigation because of simplifications resulting from the factorization of electron spin. This factorization of spin permits the use of the following basis functions[9];

$$\varphi_1 = 1s(1)\ 1s(2)$$

$$\varphi_2 = (2)^{-\frac{1}{2}} \left[1s(1)\ 2s(2) + 1s(2)\ 2s(1) \right] \qquad (38)$$

$$\varphi_3 = 2s(1)\ 2s(2)$$

where

$$1s(i) = (\pi)^{-\frac{1}{2}} (Z)^{3/2} \exp(-Zr_i)$$

$$\qquad (39)$$

$$2s(i) = (4)^{-1} (2\pi)^{-\frac{1}{2}} (Z)^{3/2} (2 - Zr_i) \exp(-Zr_i/2) \qquad ;$$

i = 1 or 2 , and Z is a scaling parameter which may be energy optimized.

The Hamiltonian, H , for the helium atom may be written in the form of Eq. (2) with

$$H_o = -(\tfrac{1}{2})\nabla_1^2 - (\tfrac{1}{2})\nabla_2^2 - Z \left[(1/r_1) + (1/r_2) \right] \qquad (40)$$

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[9] All equations and data given in this paper are in atomic units, where the unit of length is a_o , the Bohr radius, and the unit of energy is e^2/a_o .

and

$$V = (Z - 2) \left[(1/r_1) + (1/r_2)\right] + 1/r_{12} \quad . \tag{41}$$

The eigenvalues $E_k^{(o)}$, $k = 1, 2, 3$, are easily computed by applying H_o to the functions given by Eqs. (38). The matrix elements of the perturbation, V , can be computed using the tables of Roothan[10] and Barnett and Coulson[11].

To obtain the truncated reaction operator matrix elements for the $(1s)^2, (1s)(2s), (2s)^2$ ^1S states of helium we set $q = 1, 2$, and 3, respectively, in Eqs. (22), (23) and (24), and use the iterative method of solution outlined in Sec. 2[12]. In the Appendix we discuss briefly the selective nature of the iterative method of solving for the reaction operator matrix elements. It is shown that the procedure will converge (for the calculations considered in this paper) to the state under consideration regardless of the initial choice of $t_{qq}(n)$. In Table I (page 11) the $t_{kq}(n)$ are listed at several stages of approximation[13]. Each approximation is computed using one or more of the configurations $(1s)^2, (1s)(2s)$, $(2s)^2$ in the basis set. For the unscaled computations with $Z = 2$, the $t_{k1}(n)$ decrease by approximately an order of magnitude as k takes on the values 1,2, and 3 respectively. Similar trends for the $t_{kq}(n)$, with $q \neq 1$, are suggested for $k > q$ (see Table I). However with the limited data given here it is impossible to establish definite trends for these matrix elements. The $t_{kq}(n)$, for $Z = 2$, seems to be a relatively slowly varying function of n . Similar but less pronounced trends in the $t_{kq}(n)$ are seen in the energy optimized computations.

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[10] C. C. J. Roothan, J. Chem. Phys. 19, 1445 (1951).

[11] M. P. Barnett and C. A. Coulson, Phil. Trans. (Series A) 243, 221 (1951).

[12] The iterative method was carried out numerically using a Control Data Corporation 1604 computer. In the energy minimization part of the program a simple search method was employed. All data has been rounded off.

[13] The values of $t_{k\ell}(n)$, with $\ell \neq q$, are not given in this paper (see ref. 5), but are available in Tables IV, V, and VI of ref. 8. The physical significance and use of these matrix elements is at the present time unclear.

TABLE I

Truncated reaction operator matrix elements as functions of scale factor, Z, and the configurations used.

Configurations used	k	$t_{kq}(n)$ for $Z = 2$			$t_{kq}(n)$ for energy optimized Z (Z given in brackets)		
		q = 1	q = 2	q = 3	q = 1	q = 2	q = 3
$(1s)^2$	1	1.250000			(1.6875_0) 0.0000		
$(1s)(2s)$	2		0.463649			(1.8145_4) 0.0000	
$(2s)^2$	3			0.300781			(1.6992_2) 0.0000
$(1s)^2$	1	1.249061		0.070639	(1.6878_8) 0.0006_4		(1.6976_7) 0.0378_6
$(2s)^2$	3	0.037461		0.301720	0.0372_1		-0.0006_6
$(1s)^2$	1	1.169562	0.650572		(1.7565_9) 0.2313_6	(1.7267_1) 0.0916_3	
$(1s)(2s)$	2	0.105169	0.544087		0.1104_7	-0.1819_1	
$(1s)(2s)$	2		0.463208	0.032686		(1.7566_0) -0.1355_1	(1.8139_8) -0.0778_9
$(2s)^2$	3		0.018814	0.301222		-0.1014_2	0.1086_1
$(1s)^2$	1	1.169005	0.647668	0.079860	(1.7583_4) 0.2362_8	(1.6838_3) 0.0578_5	(1.8125_5) 0.0394_0
$(1s)(2s)$	2	0.105101	0.543032	0.040907	0.1140_8	-0.2848_7	-0.0764_5
$(2s)^2$	3	0.031083	0.029056	0.302394	0.0502_6	-0.1358_6	0.1078_1

Having computed the truncated reaction operator matrix elements one may compute approximations to the normalized perturbed wave functions for the $(1s)^2, (1s)(2s), (2s)^2$ ^1S states of helium using Eqs. (19), (20), and (21); these are given in Table II (page 13). For both the unscaled and energy optimized calculations the trends in the numerical values of the coefficients of the normalized perturbed wave function, $C_{kq}(n)$, are more clearly defined than those for the $t_{kq}(n)$ (compare tables I and II). The $C_{kq}(n)$ show a much smaller change in magnitude upon scaling than the $t_{kq}(n)$. Thus we conclude that the $C_{kq}(n)$ act as a "normalized" $t_{kq}(n)$. This effect is due to the energy difference, $E_q(n) - E_k^{(o)}$, appearing in the definition of the $C_{kq}(n)$ given by Eq. (20). This type of trend in the coefficients of a linear variational wave function is apparent in the work of others -- for example, the Shull and Löwdin investigation of the ground state of helium[14]. With numerical experience for atomic and molecular problems one may eventually be able to empiricize the $t_{kq}(n)$ or, equivalently, the $C_{kq}(n)$ for helium and other systems. Good estimations of the energy could then be obtained from Eqs. (17) and (36).

One can easily compute approximations to the energy of the $(1s)^2, (1s)(2s), (2s)^2$ ^1S states of helium using Eq. (17) and the $t_{qq}(n)$ obtained by the iterative procedure of Sec. 2. These energies, given in Table III (page 14), are not particularly good because of the nature of the truncated basis set used.

The approximate "effective" perturbation, $V_{eff}(q,n,Z)$, can be computed using the data of Table I (or Table II) and Eq. (25) (or Eq. (37)). As an example we give $V_{eff}(1,3,2)$ and $V_{eff}(1,3,Z_{op})$ where Z_{op} is the energy optimized Z. Defining

$$g(i,a) = (1 - ar_i)\exp(ar_i) \qquad , i=1 \text{ or } 2 \qquad (42)$$

$$V(Z) = (Z - 2)\left[(1/r_1) + (1/r_2)\right] + 1/r_{12} \qquad (43)$$

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[14] H. Shull and P. O. Löwdin, J. Chem. Phys. 30, 617 (1959).

TABLE II

Coefficients, $C_{kq}(n)$, of the configurations involved in the expansion of the normalized approximate perturbed wave functions, $\Psi_q(n)$.

Configurations used	Coefficients of configurations in Ψ_q for Z = 2.			Coefficients of configurations in Ψ_q for energy optimized Z.		
	Ψ_1	Ψ_2	Ψ_3	Ψ_1	Ψ_2	Ψ_3
$(1s)^2$	1			1		
$(1s)(2s)$		1			1	
$(2s)^2$			1			1
$(1s)^2$	0.999771		0.021390	0.9998		0.0175
$(2s)^2$	-0.021390		0.999771	-0.0174		0.9998
$(1s)^2$	0.952901	0.303280		0.9930	0.0974	
$(1s)(2s)$	-0.303280	0.952901		-0.1185	0.9952	
$(1s)(2s)$		0.999835	0.018144		0.9969	-0.0579
$(2s)^2$		-0.018144	0.999835		0.0782	0.9983
$(1s)^2$	0.952981	0.302065	0.024169	0.9922	0.0737	0.0153
$(1s)(2s)$	-0.302599	0.952848	0.022684	-0.1226	0.9923	-0.0570
$(2s)^2$	-0.016178	-0.028931	0.999451	-0.0239	0.0999	0.9983

TABLE III

Truncated reaction operator energies, $E_q(n)$, for the $(1s)^2, (1s)(2s), (2s)^2$ ^1S states of helium as functions of the scale factor, Z, and the number and kind of radially symmetric configurations included.

Configurations used	Energy for Z = 2			Energy for Optimum Z		
	E_1	E_2	E_3	E_1	E_2	E_3
$(1s)^2$	-2.750000			-2.84766		
$(1s)(2s)$		-2.036351			-2.05785	
$(2s)^2$			-0.699219			-0.72184
$(1s)^2, (2s)^2$	-2.750939		-0.698280	-2.84830		-0.72118
$(1s)^2, (1s)(2s)$	-2.830438	-1.955913		-2.85425	-2.04536	
$(1s)(2s), (2s)^2$		-2.036792	-0.698778		-2.06402	-0.71402
$(1s)^2, (1s)(2s), (2s)^2$	-2.830996	-1.956968	-0.697606	-2.85547	-2.05692	-0.71353

we obtain

$$V_{eff}(1,3,2)/V(2) = \left\{ 1-(0.079382) \left[g(1,1) + g(2,1)\right] -(0.002122)g(1,1)g(2,1)\right\}$$

$$V_{eff}(1,3,1.7583)/V(1.7583) = \left\{ \begin{array}{l} 1-(0.03090) \left[g(1,0.8792) + g(2,0.8792)\right] \\ -(0.00302)g(1,0.8792)g(2,0.8792) \end{array} \right\} \tag{44}$$

The simple form of the approximations to V_{eff} for the helium atom given above is due to the limited truncated basis set used. The use of better basis sets would permit accurate calculations of V_{eff}. After sufficient numerical and theoretical experience we hope it will be possible to accurately empiricize V_{eff} for many atomic and molecular problems.

One of the most useful aspects of the reaction operator formulation is that the operator, t , takes into account all interactions of the system above the unperturbed state. Thus t and its matrix elements (and of course V_{eff} and its matrix elements) must give valuable information concerning the physical properties of the perturbed system.

Acknowledgement

Appendix.   <u>Convergence Properties of the Iterative Method of Solving</u>
<u>for the Reaction Operator Matrix Elements.</u>

In the computations outlined in Sec. 4., interesting convergence properties of the iterative method for obtaining the reaction operator matrix elements were apparent. The method converged to the $t_{qq}(n)$ corresponding to the state under consideration even if the initial guess for $t_{qq}(n)$ corresponded to the solution for another perturbed state. In the following discussion we make use of a theorem[6] which states: If the equation, $x = f(x)$ subject to the condition $f'(x) \neq 0$, is solved by the iterative procedure, $x_{K+1} = f(x_K)$, then the method will converge to a particular root λ , if $|f'(\lambda)| < 1$. If $|f'(\lambda)| > 1$, the iterative procedure will diverge from the root λ .

Using Eq. (22) with $q = 1$; $Z = 2$; $s = 1,2$, or 3; one can show[8] that for the ground state

$$t_{11}(3) = V_{11} + v_{12}^2 \left[\Upsilon_{12} - v_{23}^2/\Upsilon_{13} \right]^{-1} \tag{45}$$

$$+ v_{13}^2 \left[\Upsilon_{13} - v_{23}^2/\Upsilon_{12} \right]^{-1} + 2v_{12}v_{23}v_{31} \left[\Upsilon_{12}\Upsilon_{13} - v_{23}^2 \right]^{-1}$$

where

$$\Upsilon_{1j} = E_1^{(o)} - H_{jj} + t_{11}(3) \quad , \; j=2,3 \; . \tag{46}$$

If $E_1^{(o)}$ is added to both sides of Eq. (45) we obtain the Feenberg perturbation series[15] for a basis set comprised of three real orthonormal eigenfunctions of H_o . Equation (45) has the form $t_{11} = f(t_{11})$. Using Eq. (45) one obtains:

$$f'(t_{11}(3)) = \left[\begin{array}{c} v_{12}^2 v_{23}^2 + v_{13}^2 v_{23}^2 + v_{12}^2 \Upsilon_{13}^2 \\ + v_{13}^2 \Upsilon_{12}^2 + 2v_{13}v_{32}v_{21}(\Upsilon_{12} + \Upsilon_{13}) \end{array} \right] \left[\begin{array}{c} \Upsilon_{12} \Upsilon_{13} \\ -v_{23}^2 \end{array} \right]^{-2} . \tag{47}$$

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[15] E. Feenberg, Phys. Rev. <u>74</u>, 206 (1948).

The roots of Eq. (45), $t_{11}^{(j)}(3)$, which correspond to the j-th perturbed state can be calculated by the following equation:

$$t_{11}^{(j)}(3) \;=\; E_j(3) - E_1^{(o)} \qquad , \; j=1,2,3 \; . \tag{48}$$

The values for $\left| f'(t_{11}^{(j)}(3)) \right|$, $j = 1,2,3$, are given below:

$$\left| f'(t_{11}^{(1)}(3)) \right| \;=\; 0.1011$$

$$\left| f'(t_{11}^{(2)}(3)) \right| \;=\; 9.960 \tag{49}$$

$$\left| f'(t_{11}^{(3)}(3)) \right| \;=\; 1.71 \times 10^3$$

Equations (49) explain the selective nature of the iterative procedure for the ground state calculations with $Z = 2$, $n = 3$. Similar explanations[8] can be given for the other computations of Sec. 4.